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NONE

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C2C

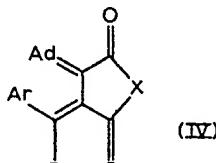
(71) Applicant: HAROLD  
GEORGE HELLER, 11  
ERWGOCH,  
WAUNFAWR,  
ABERYSTWYTH,  
DYFED, SY23 3AZ,  
WALES

(72) Inventor:  
HAROLD GEORGE  
HELLER

(74) Agents: BROOKES &  
MARTIN

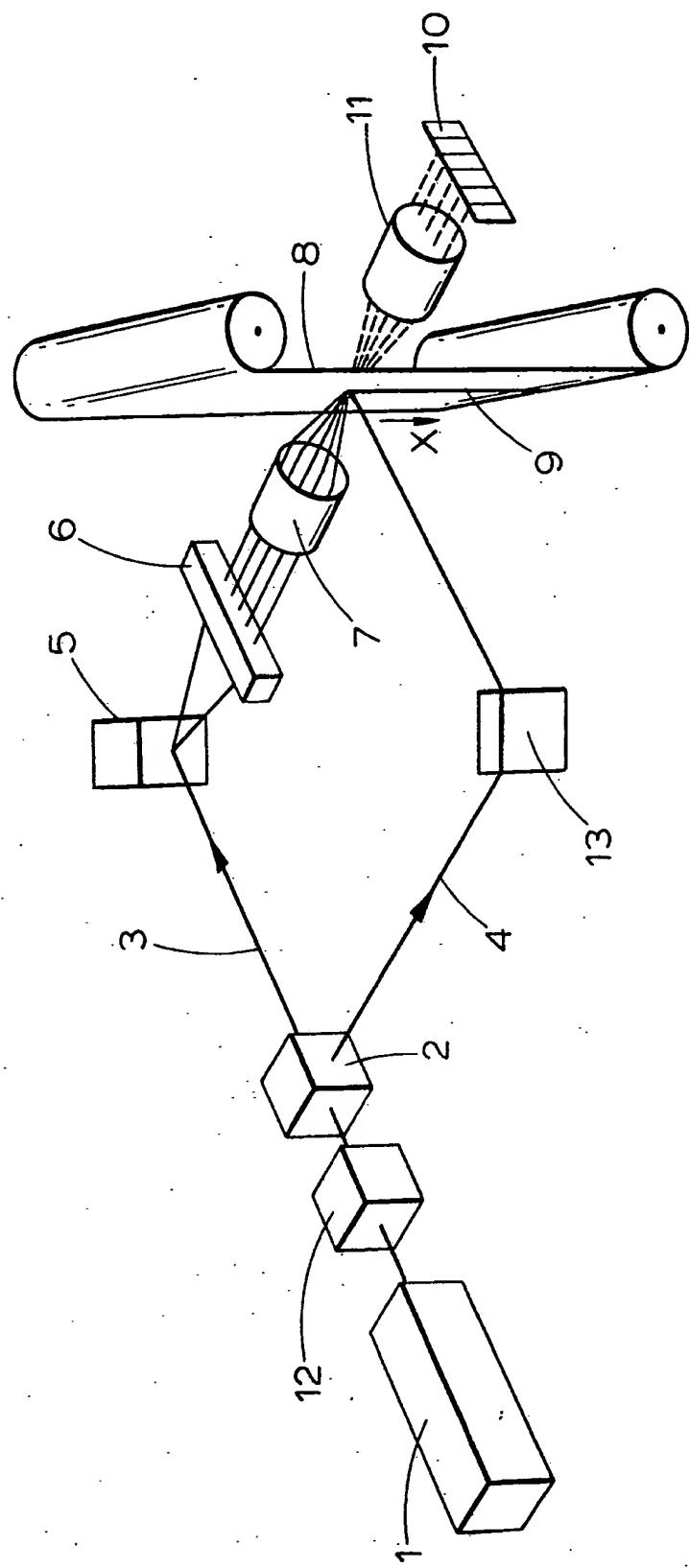
(54) PHOTOCROMIC  
ADAMANTYLIDENE-SUCCINIC  
ANHYDRIDE AND -  
SUCCINIMIDE COMPOUNDS

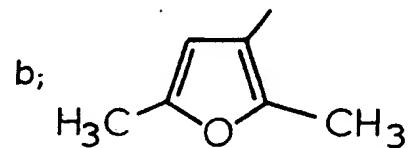
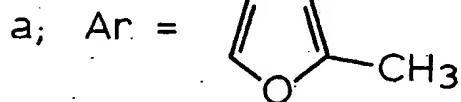
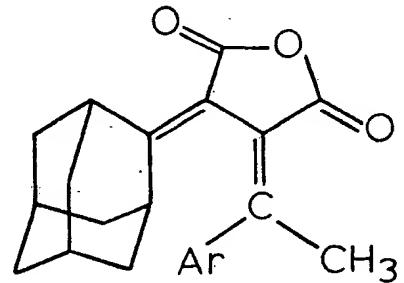
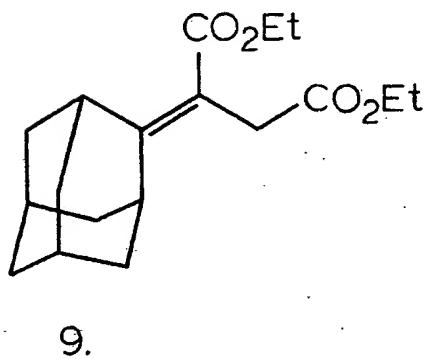
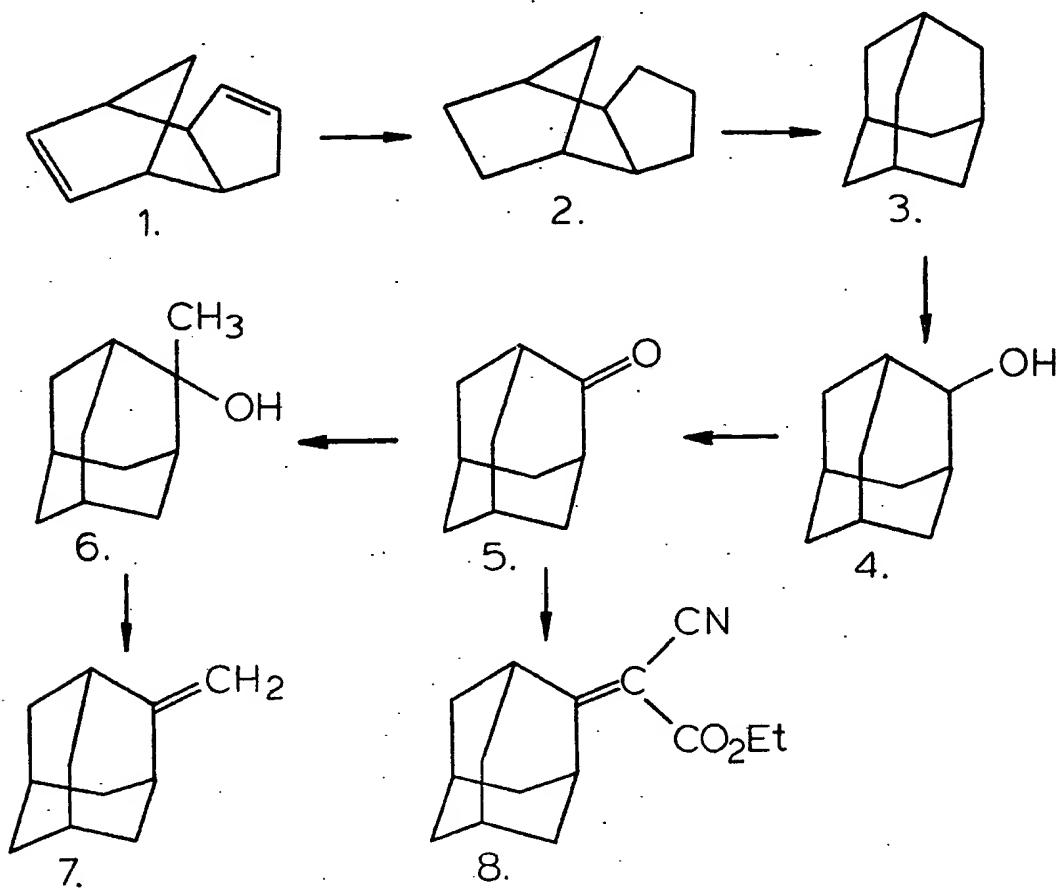
(57) Novel photochromic  
adamantylidene-succinic anhydride  
and -succinimide derivatives of the  
formula



wherein X represents oxygen or  $>NR_6$ ,  
R<sub>6</sub> being hydrogen or an alkyl, aryl or  
aralkyl group; R represents hydrogen  
or an alkyl, aryl, aralkyl or hetero-  
cyclic group; Ar represents a 3-furyl,  
3-thienyl, 3-benzofuryl or 3-benzo-  
thienyl group, or a phenyl group  
containing a *m*-alkoxy or -aryloxy  
substituent; and Ad represents an  
adamantylidene group; are prepared  
from novel adamant-2-ylidene dialkyl  
succinate esters. The novel photo-  
chromic compounds are capable of  
undergoing a very large number of  
colour change cycles on exposure to  
activating radiation and are especially  
useful when coated onto films or discs  
for holographic data recording.

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## SPECIFICATION

## PHOTOCHROMIC COMPOUNDS

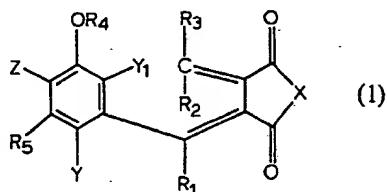
This invention relates to compounds which exhibit photochromism and to their use in

5 recording and display devices.

Photochromism can be defined as the ability of a material to change its visible absorption spectrum on exposure to activating radiation and to revert to its original absorption spectrum on removal of the 10 activating radiation or on substituting radiation of a different wavelength.

In British Patent Specification No. 1,442,628 there is described a series of substituted phenyl-methylene succinic anhydrides and succinic imides 15 which exhibit marked photochromic properties and which possess good thermal stability and have a reduced tendency to undergo irreversible side reactions on photoactivation as compared with previously known photochromic compounds.

20 Photochromic compounds of the series described in the above prior specification have the general formula:



wherein

25 X represents oxygen or  $>NR_6$ ,  $R_6$  being hydrogen, alkyl, aryl or aralkyl,

$R_1$  represents hydrogen, alkyl, aryl or aralkyl,

Y and  $Y^1$  are the same or different and represent hydrogen, alkyl, halogen or alkoxy,

30 Z represents hydrogen, halogen, alkyl, alkoxy or aryloxy,

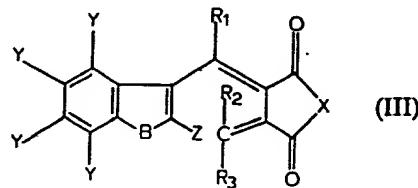
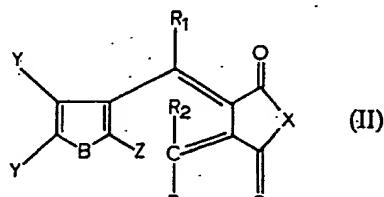
$R_2$  represents hydrogen, alkyl, alkoxy or aryloxy,

$R_4$  represents alkyl, aryl or aralkyl and  $R_2$  and  $R_3$

35 represent the same or different alkyl or aryl groups or one of  $R_2$  and  $R_3$  represents hydrogen and the other is alkyl, aryl or aralkyl with the proviso that when Z or Y is alkoxy or aryloxy,  $R_1$  is other than hydrogen.

40 A further series of relates photochromic compounds, in which the phenyl group is replaced by a furan, benzofuran, thiophene or benzo(b)thiophene nucleus is disclosed in British Patent Specification No. 1,464,603.

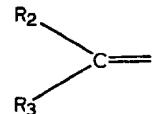
45 The compounds disclosed in specification No. 1,464,603 have one of the following general formulae:



50 in which X represent oxygen or  $NR_6$  where  $R_6$  represents hydrogen, alkyl having 1 to 20 carbon atoms, cycloalkyl having 5 to 12 carbon atoms, aralkyl having 7 to 9 carbon atoms, aryl having 6 to 14 carbon atoms, which may be substituted with 1 or more halogen or alkoxy groups having 1 to 20 carbon atoms, or alkaryl having 7 to 22 carbon atoms; B represents oxygen or sulphur;  $R^1$  represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 14 carbon atoms:  $R^2$  and  $R^3$  are the same or different alkyl groups having 1 to 20 carbon atoms or one of  $R^2$  and  $R^3$  is hydrogen and the other is an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 14 carbon atoms which may be substituted with one or more halogen atoms and/or any combination of groups selected from the following alkoxy groups having 1 to 20 carbon atoms, or alkaryl having 7 to 22 carbon atoms; or is a methylenedioxy group, Z represents hydrogen, 70 an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 14 carbon atoms or an aralkyl group having 7 to 20 carbon atoms; each Y is the same or different and represents a hydrogen or halogen atom, an alkyl or alkoxy group having 1 to 20 carbon atoms, or an aryl or aryloxy group having 6 to 14 carbon atoms.

These heterocyclic compounds exhibit additional improvements in thermal stability and in the ability to undergo a very large number of 80 colour change cycles without substantial deterioration in the character of the absorption spectra, as a result of formation of so-called fatigue products of irreversible side reactions.

It has now been discovered that improvements 85 in the degree of photosensitivity products are obtained by replacing the



group in the above two general formula with an adamantylidene group.

90 According to the present invention therefore there is provided a series of photochromic compounds of the general formula (IV)

wherein  
95 X represents oxygen or  $NR_6$ ,  $R_6$  being

hydrogen or an alkyl, aryl or aralkyl group;

R represents hydrogen or an alkyl, aryl, aralkyl or heterocyclic group;

Ar represents a 3-furyl, 3-thienyl group, 3-benzofuryl or 3-benzothienyl group or a phenyl group containing a meta alkoxy or aryloxy substituent; and

Ad represents an adamantylidene group.

Adamantane, the root hydrocarbon is a tricyclo-decane having a rigid, strain free cage structure, whose synthesis from dicyclopentadiene is described by Schleyer et al in *Organic Synthesis*, 1962, volume 42, page 8. Referring to the accompanying formula drawings, the synthesis involves hydrogenation of dicyclopentadiene (1) to endo-tetrahydridocyclopentadiene (2) and rearrangement of the latter using a catalyst comprising anhydrous aluminium chloride and hydrogen chloride to adamantane (3).

Adamantan-2-ol(4) can be prepared by free radical hydroxylation of adamantane using peracetic acid and U.V. radiation (Schleyer et al. *JACS*, 1961, 83, p.182) and the product oxidised to Adamantan-2-one (5) using a chromic acid/sulphuric acid mixture. More convenient methods of preparing adamantanone by direct oxidation of adamantane are described in U.S. patent 3,257,456 and Geluk et al *Organic Synthesis*, 1973, Volume 53, p.8.

Adamantan-2-one reacts with methyl magnesium bromide to yield 2-methyladamantan-2-ol (6) which, on heating with 85% phosphoric acid, gives exclusively 2-methylenadamantane (7) (Schleyer et al. *JACS* paper cited above).

Photochromic compounds in accordance with the invention may be prepared by a Stobbe condensation reaction. (Chapter 1 of volume 6 of "Organic Reactions"), Wiley, New York, 1951. Thus adamantan-2-one is refluxed with a succinate diester in a solution of potassium t-butoxide in t-butanol to give the potassium salt of the corresponding half ester. Boiling in a benzene/ethanol mixture containing concentrated hydrochloric acid yields adamant-2-ylidene-succinate diester. These diesters are novel intermediates and the structure of the diethyl ester is formula (9) of the accompanying drawings.

Compounds of formula (IV) can be obtained by reacting the intermediate (9) with an appropriate aldehyde or ketone in the presence of sodium hydride. Formula (10) of the accompanying drawings shows the structure of two specific compounds in accordance with the invention whose preparation is described in the worked Examples below.

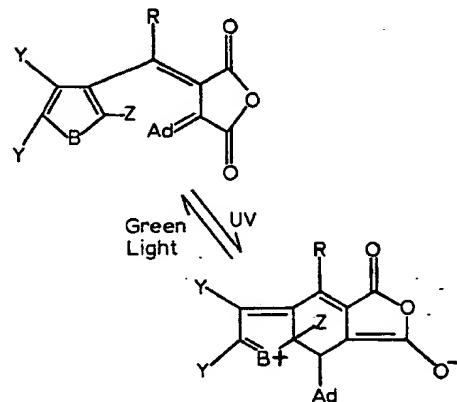
The corresponding succinimides, in which X in formula (IV) is  $NR_6$  and  $R_6$  is other than hydrogen, can be prepared by reacting the succinic anhydride with a primary amine or by using a compound of the formula:—  $R_6 NHMgBr$  as described in my above cited prior British patent specifications.

Succinimides in which X is  $>NH$  may be prepared by reacting the appropriate succinic anhydride with concentrated ammonia to produce

the corresponding half amide acid and then reacting the product with diazomethane to yield the methyl ester of the half amide, followed by cyclisation using sodium ethoxide. This procedure is described by Goldschmidt et al in *Leibigs Annalen der Chemie*, 1957, volume 604, page 121.

Reversible photocyclisation takes place when compounds of the formula (IV) are exposed to activating radiation, normally in the near ultraviolet range, e.g. about 330—400 nm. The coloured forms frequently possess a deep red colour and the reversion to the original form can normally be achieved by exposure to white light.

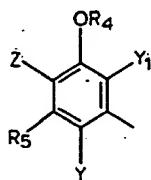
It is believed that the photocyclisation reaction involves formation of a linkage between the  $\alpha$ -carbon atom of the adamantane ring and the 2 position of the radical in the Ar position of formula (IV) and migration of the double bonds in the resulting ring system to form a chain of conjugated double bonds extending from a carbonyl oxygen atom of the succinic anhydride residue to a heteroatom in the Ar radical, or to an alkoxy or aryloxy group, where the Ar radical is a phenyl radical. The reversible photocyclisation reaction is illustrated by the following theoretical reaction scheme, in the case of certain compounds falling within the scope of formula (IV):—



A preferred class of photochromic compounds falling within formula (IV) are those in which Ar represents a 3-furyl, a 3-benzofuryl, a 3-thienyl or a 3-benzothienyl group since it has been found that such compounds possess deeply coloured cyclic forms and a very rapid rate of photochemical reversal. Additionally these compounds are very stable and exhibit a very low degree of fatigue. The heterocyclic ring may contain substituents such as Y and Z as defined above in connection with formulae (II) and (III).

It is believed that the very marked improvements in desirable photochromic properties exhibited by the compounds of the present invention arise from the stable character of the adamantane ring, which possesses a structure free from both angle and conformational strain and in which bond migration does not occur.

A further class of photochromic compounds included within the scope of the present invention are those having the formula (IV) in which Ar represents the radical:—

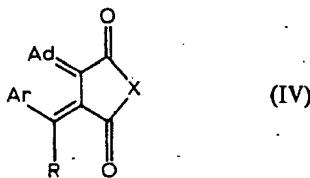


in which R<sub>4</sub>, R<sub>5</sub>, Y and Y<sub>1</sub> have the significance stated above in connection with formula (I). In the case of this class of compounds, R in formula (IV)

5 may be hydrogen provided that neither Z nor Y in the above radical is alkoxy or aryloxy.

The compounds of the invention are useful in display and recording devices, particularly holographic data recording and storage systems.

10 According to a further aspect of the present invention, there is provided a holographic data recording and storage method which comprises producing a holographic record using coherent visible light by interfering a reference beam and a data beam in the plane of the surface of the material, whereby a series of holograms 15 embodying data recording from said data beam are formed, said photochromic material comprising a substrate having coated hereon or dispersed therein a photochromic compound of the general formula (IV):—



wherein

X represents oxygen or >NR<sub>6</sub>, R<sub>6</sub> being 25 hydrogen or an alkyl, aryl or aralkyl group; R represents hydrogen or an alkyl, aryl, aralkyl or heterocyclic group; Ar represents a 3-furyl, 3-thienyl group, 3-benzofuryl or 3-benzothienyl group, or a phenyl 30 group containing a meta alkoxy or aryloxy substituent; and

Ad represents an adamantylidene group.

Preferably R in formula (IV) above represents a lower alkyl (e.g. having 1 to 6 carbon atoms), a 35 phenyl, naphthyl or alkylphenyl group. It is also preferred that Ar in formula (IV) above is a 3-furyl, 3-thienyl, 3-benzofuryl or 3-benzothienyl group.

Preferably, the recording material is initially converted to the coloured form by irradiation with 40 ultra-violet light and the hologram recorded on the coloured material by bleaching. Formation of the hologram by bleaching (i.e. by conversion of the photochromic compound from its cyclic to non-cyclic form) is advantageous since it enables the 45 powerful emission lines of the argon ion laser at 488 or 514 nm to be used for writing the data. The term 'bleaching' is used to describe this conversion, although in some cases the photochromic compound may have a pale colour 50 in its non-cyclic form.

Conversion of the compound to its coloured state may be achieved by off line exposure to a

U.V., e.g. mercury vapour lamp or, in the case where an argon ion laser is used, by operating the 55 laser simultaneously in the visible and U.V. ranges and directing the U.V. beam onto the photochromic surface so as to activate the surface prior to writing the data by bleaching.

Apparatus for holographic data storage in 60 accordance with the invention is illustrated by the accompanying diagrammatic drawing.

Referring to the drawing, a water-cooled argon ion laser 1 is operated to produce a beam of 488 mm or 515 nm wavelength at an output of about 2 65 watts. The output beam is divided by a beam splitter 2 into a beam 3 (termed the data beam) and a beam 4 (termed the reference or replay beam). Beam 3 is directed by a further beam splitter 5 onto a page composer 6 of conventional construction. The page composer is an array of light operated shutters and preferably is of the PLZT type i.e. an array of lanthanum doped lead 70 zirconate titanate electrodes bonded to a block of glass. Lens 7 focusses the beam onto the photochromic surface which, as in the illustrated embodiment, is a film 8 coated with a photochromic compound in a manner described below. Beam 4 is directed onto the film by a mirror 13. A 75 hologram 9 is formed on the surface of the film by interference of the data beam with the reference beam.

The film 8 is transported through the apparatus by means not shown in the direction of the arrow X. As indicated above, data is preferably written 85 on the film by bleaching the coloured form of the photographic compound. While the film can be treated off line with U.V. light to convert it to its coloured form, it is usually preferable to simultaneously operate the laser 1 in the visible 90 and U.V. range and provided a suitable optical path to direct a U.V. beam onto the film so that selected data or blocks of data can be erased and/or rewritten.

In operation, the page composer 6 is controlled 95 by electrical input signals which correspond with the data to be recorded. Thus a pattern of light beams is produced by the composer each of which carries the encoded data applied electrically to the page composer. These beams when focussed onto

100 the film 9 interfere with the reference beam 4 to produce a hologram track which can be read out as described below. A higher data recording density can be achieved by a known technique called multiplexing in which a series of 105 overlapping sub-hologram tracks are formed. This is achieved by deflecting the data and reference beams transversely of the film using scanning means such as mirrors rotated by a stepping motor.

Read out of the hologram is effected by 110 switching off the data beam and using the reference beam to illuminate the hologram and focussing the image on a photodiode array 10 via a lens 11. Surprisingly, read out of the hologram can be achieved using light of the same intensity as that 115 used for recording without substantial loss of the recorded image. However, the level of destructive read out can be reduced to an insignificant level by

reading out the holograms at a wavelength outside the visible absorption band of the photochromic compound, for example at a wavelength of 632 nm using a neon ion laser. Usually it is more

5 convenient to read out at the same wavelength as recording but at a lower intensity.

It will be appreciated that the recording and retrieving of data can be carried out simultaneously or at different times.

10 The accompanying drawing also shows a clock modulator 12 which enables correct synchronism of the recorded data and its correct retrieval.

Preferably, the photochromic compounds are coated onto or incorporated within a light-

15 transmissive support using a suitable binder. One convenient method is to dissolve the photochromic compound in a common solvent for the binder and the compound and coat the solution onto a suitable support using conventional

20 coating procedures, followed by drying to remove the solvent. It has been found that best results are achieved using non-halogenated solvents and plastics binders which have a low permeability towards oxygen, e.g. polyesters and

25 polycarbonates. The support can be in any desired form, e.g. as tapes, discs, plates or screens.

The following Examples are given to illustrate the invention and the manner in which it may be carried into effect.

30 EXAMPLE 1.

(i) Preparation of diethyl adamant-2-ylidenesuccinate (9)

Adamantan-2-one (50 parts) and diethyl succinate (58 parts) in t-butanol (200 parts by volume) were added to a solution of potassium t-butoxide in t-butanol (prepared by dissolving potassium (13.5 parts) in t-butanol (700 parts by volume). The reaction mixture was boiled (24h), cooled, and the solid filtered off and extracted

35 with ether. The ether extracted gave adamantanone (20 parts). The ether-insoluble solid, the potassium salt of the itaconic half ester, was dissolved in water and acidified with 5M hydrochloric acid, giving ethyl adamant-2-ylidene-

40 succinate (50 parts), m.p. 85—87°C. 82% yield based on adamantan-2-one consumed.

The half ester was boiled with ethanol (75 parts by volume), benzene (225 parts by volume) and conc. hydrochloric acid (2 parts by volume) and

45 the water azeotroped off using a Dean and Stark apparatus. Unchanged half ester was extracted with sodium carbonate solution, the organic layer was dried (magnesium sulphate), filtered and the solvent removed. The diester was obtained as a

50 colourless oil (47 parts) 86% yield.

(ii) Preparation of adamant-2-ylidene (2'-methyl-3'-furyl) ethylidene succinic anhydride (10a)

2-Methyl-3-acetylfuran (11 parts) and diethyl adamant-2-ylidene succinate (27 parts) in toluene (100 parts by volume) was added slowly to a stirred suspension of sodium hydride (50% dispersion in oil) (9 parts) in toluene (100 parts by volume). The reaction mixture was stirred (1h) until evolution of

55 hydrogen had ceased and then the temperature of the reaction mixture was raised to 30°C and stirred for a further hour. The reaction mixture was cooled, poured onto crushed ice, and the toluene layer separated, extracted with 2M sodium hydroxide and the alkaline extracts combined. The latter was acidified with conc. hydrochloric acid and the liberated oil extracted with toluene, dried and solvent removed. The residual oil was boiled (1h) with potassium hydroxide (15 parts) in 2-propanol (200 parts by volume). The solution was

60 cooled and the dipotassium salt filtered off, dissolved in water, and acidified with conc. hydrochloric acid. The diacid which separated was extracted into ether, dried (magnesium sulphate) and ether removed. The diacid was boiled (1h)

65 with acetyl chloride (175 parts by volume) and the acetyl chloride removed. The residual oil was triturated with ether and the resulting solid, Soxhlet extracted with petroleum b.p. 60—80°C. Removal of the petrol left a solid which was

70 crystallised from 1:3 mixture by volume of chloroform and petroleum b.p. 60—80°C. giving the anhydride in nearly colourless crystals, m.p. 197—198.5°C, which turn deep red on irradiation at 366 nm. The colour is reversed by white light.

75 EXAMPLE 2.

Preparation of adamant-2-ylidene-(2',5'dimethyl-3'-furyl) ethylidenesuccinic anhydride (10b)

The procedure described in part (ii) of Example 1 was repeated using 2,5-dimethyl-3-acetylfuran (7 parts) and diethyl adamant-2-ylidenesuccinate (15 parts) in toluene and sodium hydride (50% dispersion in oil) (5.3 parts) in toluene. The anhydride separated from ether and was

80 crystallised from petroleum 60—80°C, giving colourless needles, m.p. 177—179°C, which turn dark red on irradiation at 366 nm. The colour is reversed by white light.

85 The structure of the intermediate and of the final products of the above two Examples is shown in the attached drawings, formulae (9), (10a) and (10b).

The following Examples are given to illustrate the preparation of a coated film or screen in accordance with the invention.

90 EXAMPLE 3.

10 grams of the compound (10a) prepared in Example 1 were dissolved, together with 100 grams of cellulose acetate, in 1 litre of a 50/50 volume mixture of 2-hydroxy ethyl acetate and acetone.

95 The resulting solution was filtered and coated onto a polyester base sheet using a blade over roller coating technique to achieve a wet coating thickness of 120 microns. After drying at 120°C, the coating had a dry thickness of about 12

100 microns. The resulting sheet produced a deep red image when exposed to U.V. light having a wavelength of 366 nm, the image being bleached by subsequent exposure to a light beam at 550 nm and could be used as a holographic recording

105 material or as a display screen. Screens of higher optical quality can be produced using glass plates in place of polyester film.

**EXAMPLE 4.**

The compound obtained in Example 2 (10b) (50mg) was dissolved in 5 grams of a polyester glass by heating to 100°C. and stirring continuously.

5 The molten solution was then sandwiched between 2½" x 2" glass plates which were separated by 20 µm spacers. The whole was evacuated to remove trapped air bubbles and allowed to cool to form a solid film. A dark red image could be produced by

10 impinging a beam of U.V. light on the film, which was bleached with an argon ion laser beam at 550 nm. The film had a higher optical quality than that produced in Example 3 and could be used for holographic recording medium or as a display

15 device.

**EXAMPLE 5.**

A solution of the photochromic compound prepared in Example 1 was obtained by dissolving 10 grams in 1 litre of toluene with warming. A

20 piece of "Wratten" 50 grade paper was dipped into the solution, removed and dried in air at room temperature. A deep red colouration was obtained by exposing the impregnated paper to U.V. light and the paper could be bleached with visible light.

25 The impregnated paper was suitable for making temporary copies e.g. from microfiche, under normal ambient conditions.

While the foregoing description has concentrated on the use of the photochromic

30 compounds in holographic data recording, it will be appreciated that they may also be used in the production of films and screens for recording and display purposes generally. Some of the other applications are summarized below:—

**35 Photography and Reproduction systems:**

Films or plates may be prepared by coating a support with a solution, dispersion or emulsion containing a compound or mixture of compounds in accordance with the invention. The resulting

40 films or plates can be used as temporary positives or negatives without any need for development or fixing from which permanent prints can be made using conventional photographic materials. The image can be erased and the same photochromic

45 film or plate re-used repeatedly.

Reproduction and copying using plate or films are of particular value in making temporary copies e.g. from microfiche or to prepare a temporary master.

**50 Photochromic display systems:**

Photochromic screens can also be used as information boards, e.g. at railway stations or airports or in special display systems such as flight simulators. The information can be written on the

55 boards with a scanning or laser or other light beam device and subsequently erased or updated.

The formation of the coloured cyclic structure is stimulated most effectively by exposure of the compounds to light in the near ultra-violet range,

60 e.g. at about 330—400 nm. For most of the

applications described above it will be necessary or desirable to remove the image at a faster rate than the natural fading rate and this is readily achieved by exposure to light in the visible spectrum,

65 preferably green light in the range of about 514—550 nm, which can be obtained using an argon ion laser.

In some cases the formation of the coloured cyclic structure may be induced by heat. Thus it

70 has been found that compounds in which there is no substituent in the 2-position of the furyl or thienyl ring will undergo rapid ring closure to the coloured form on heating to above 100°C, preferably to about 140°C. The cyclised product is

75 thermally stable but the cyclisation reaction can be reversed using white light and both forms of the compound are stable in the dark at room temperature.

The second group of applications make use of

80 the reduced light transmission properties of the coloured forms of the compounds. Thus photochromic packaging film (e.g. coated cellophane) can be used as an outer wrapper to protect products from the effects of sunlight, while

85 allowing the products to be viewed through the wrapping in artificial light. Perishable foodstuffs and pharmaceuticals are examples of products which may be advantageously protected in this way.

90 Similarly, shop windows or storage cabinets may be treated with the compounds of the invention so as to protect their contents. Paints can be formulated with the photochromic compounds so as to reduce the penetration of sunlight, thereby

95 reducing dazzle and extending the life of the paint film.

Because many of the compounds of the present invention exhibit a high degree of conversion into the coloured form, possess a high degree of

100 thermal stability and negligible photochemical fatigue, the compounds are well suited for use as chemical light meters. Thus they can be used to indicate a minimum light intensity or to detect U.V. light. Continuous monitoring of U.V.

105 radiation flux enables assessment of atmospheric pollution levels and monitoring of U.V. radiation in sunlight is of value in the current endeavours to utilize solar energy directly.

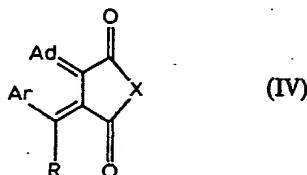
For the above uses, the photochromic

110 compounds are normally dispersed in a light transmissive vehicle to form a solution, emulsion or dispersion and then applied as a coating to a support, after which the continuous phase is removed. Alternatively the compounds may be

115 incorporated within or impregnated into a support, which may be a plate, film, fabric, paper or sheet. Further alternative presentations are as a solid polycrystallite coating, as a large single crystal or as a fluid solution in a cell.

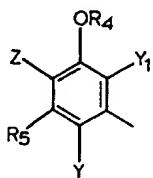
**120 CLAIMS**

1. A photochromic compound of the general formula:—



wherein

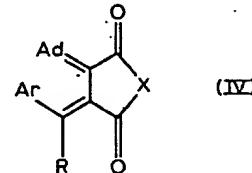
- X represents oxygen or  $>NR_6$ ,  $R_6$  being hydrogen or an alkyl, aryl or aralkyl group;
- 5 R represents hydrogen or an alkyl, aryl, aralkyl or heterocyclic group;
- Ar represents a 3-furyl, 3-thienyl group, 3-benzofuryl or 3-benzothienyl group, or a phenyl group containing a meta-alkoxy or aryloxy substituent; and
- 10 Ad represents an adamantylidene group;
- 2. A compound according to claim 1 in which Ar represents a phenyl group which contains alkoxy or aryloxy substituents in both meta positions, the phenyl ring being unsubstituted in its other positions or contains substituent groups other than alkoxy and aryloxy groups.
- 15 3. A compound according to claim 1 in which R represents an alkyl, aryl or aralkyl group.
- 20 4. A compound according to claim 1 in which Ar represents the phenyl radical:—



wherein

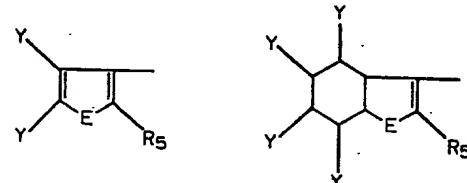
- R<sub>4</sub> represents alkyl, aryl or aralkyl;
- 25 Z represents hydrogen, halogen, alkyl, alkoxy or aryloxy;
- R<sub>5</sub> represents hydrogen, alkyl, alkoxy or aryloxy;
- Y and Y<sub>1</sub> are the same or different and represent hydrogen, deuterium, alkyl, halogen or alkoxy, with the proviso that R is other than hydrogen unless R<sub>4</sub> is alkyl or aryl and R<sub>5</sub> is alkoxy or aryloxy and none of Z, Y and Y<sub>1</sub> represent alkoxy or aryloxy.
- 30 5. A photochromic compound of the general formula (IV) set forth in claim 1 wherein X represents oxygen or  $>NR_6$ ,  $R_6$  being hydrogen or an alkyl, aryl or aralkyl group;
- R represents an alkyl, aryl or aralkyl group;
- 35 A represents a 3-furyl, 3-thienyl group, 3-benzofuryl or 3-benzothienyl group; and
- Ad represents an adamantylidene group.
- 40 6. An adamant-2-ylidene dialkyl succinate ester.
- 7. A holographic data recording and storage
- 45 method which comprises producing a holographic record using coherent visible light by interfering a reference beam and a data beam in the plane of the surface of the material whereby a series of holograms embodying data recorded from said
- 50 data beam are formed, said photochromic material comprising a substrate having coated thereon or

dispersed therein a photochromic compound of the general formula (IV):—



55 wherein

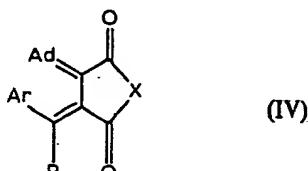
- Z represents oxygen or  $>NR_6$ ,  $R_6$  being hydrogen or an alkyl, aryl or aralkyl group;
- R represents hydrogen or an alkyl, aryl, aralkyl or heterocyclic group;
- 60 Ar represents a 3-furyl, 3-thienyl group, 3-benzofuryl or 3-benzothienyl group, or a phenyl group containing a meta alkoxy or aryloxy substituent; and
- Ad represents an adamantylidene group.
- 65 8. A method according to claim 7 in which the group represented by Ar in formula (IV) is a group of the formula:—



70 wherein E represents oxygen or sulphur; each Y is independently selected from hydrogen, halogen, alkyl, aryl, aralkyl, alkoxy and aryloxy groups; and R<sub>5</sub> represents hydrogen or an alkyl, aryl or aralkyl group.

- 9. A method according to claim 7 or 8 in which the photochromic material is supported on a film or disc which is moved relatively to the data and reference beams.
- 75 10. A method according to claim 9 in which the hologram track is formed in a pattern of overlapping sub-holograms, thus increasing the packing density of the surface.
- 80 11. A method according to any one of claims 7 to 10 in which the photochromic compound is converted to its coloured form as a preliminary step separate from the holographic recording apparatus.
- 85 12. A method according to any one of claims 7 to 11 in which the hologram is recorded using visible light emitted from an argon ion laser of a wavelength in the range of 514 to 550 nm.
- 90 13. A method according to any one of claims 7 to 12 in which the photochromic compound is converted to its coloured form using U.V. light generated by a laser.
- 95 14. A method according to claim 13 in which the same laser is used to generate the U.V. light and the visible light.
- 15. A photochromic image recording or display device which comprises a photochromic compound having the general formula (IV) below in the form of a coating on a support or dispersed

in a light-transmitting matrix:—



wherein X represents oxygen or >NR<sub>6</sub>, R<sub>6</sub> being hydrogen or an alkyl, aryl or aralkyl group;

5 R represents hydrogen or an alkyl, aryl, aralkyl or heterocyclic group;

Ar represents a 3-furyl, 3-thienyl group, 3-benzofuryl or 3-benzothienyl group, or a phenyl group containing a meta alkoxy or aryloxy

10 substituent; and

Ad represents an adamantylidene group.

16. A display or recording device according to claim 15 in which the support is a light transmitting material in the form of a disc or film and the

15 photochromic compound is dispersed in a plastics coating applied to the support.

17. A display or recording device according to claim 15 or claim 16 in which the plastics coating has a low permeability towards oxygen.

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